



CLEAN

VERSION

07875/0200146-US0

FLAME RETARDANT POLYMER COMPOSITION

Description

5 The invention relates to a flame retardant polymer composition and to a process of producing a flame retardant agent.

10 In the construction, furniture, transport or electrical industry and in the electronics industry, plastics are used as materials. For many applications, polymers have to comply with national or international flame retardant standards. As most polymers, in themselves, are combustible, they have to be modified to be classified as being flame
15 retardant. In general, this is achieved by adding organic or inorganic flame retardant agents. Within a multitude of different flame retardant agents, metal hydrates, more particularly those of aluminium, have become very important (G. Kirschbaum, Kunststoffe, 79, 199, pp 1205-1208, and R.
20 Schmidt, Kunststoffe, 88, 1998, pp 2058-2061).

The flame retardant effect of the aluminium hydroxide is based on the thermal splitting-off of the chemically bonded water between 200 - 400 °C. In the course of said
25 endothermic decomposition of the hydroxide, energy is

consumed and as a result, the surface of the plastic material is cooled. In addition, the released water vapour dilutes the combustible organic degradation products of the polymers. The aluminium oxide remaining as residue adsorbs polycyclic aromatic compounds which are formed when burning the polymer matrix. As these compounds are constituents of black smoke, aluminium hydroxide also contributes to a reduction of smoke density in the case of fire. Therefore, when using the non-poisonous and halogen-free aluminium hydroxide it is possible to produce halogen-free polymer compounds which are low in smoke production.

The disadvantage refers to the large quantities of aluminium hydroxide which have to be present in plastics to be able to comply with the various standards referring to flame retardant materials. Because of said large quantities, the processing methods for such flame retardant polymer mixtures, such as extrusion, are difficult and the mechanical properties of said compounds are often inadequate.

The achievable extrusion speed while coating copper veins or while applying the cable sheathing to a cable structure constitutes an important cost factor of cable production. Polymer compounds filled with finely precipitated aluminium hydroxides which, in addition to meeting standard electrical, mechanical and flame retardant requirements, permit a high extrusion speed are crucial for halogen-free flame retardant cables to gain market share compared to alternative technologies.

One possibility of achieving further improvements consists in applying a layer of organic additives, e.g. silanes or titanates to the aluminium hydroxide surface. If said coated aluminium hydroxides are mixed into thermoplastics,
5 it is possible to achieve higher extrusion speeds.

It is the object of the invention to provide a polymer composition which is filled with standard large amounts of fine-precipitated aluminium hydroxide and which does not
10 have the above-described disadvantages, but which, with filler levels up to 80%, can still be easily processed. Compared to coating methods, the production method is simple and cost-effective.

15 Said objective was achieved by using fine-precipitated aluminium hydroxide which is subjected to a special mill drying process. The mill drying unit consists of a rotor which is firmly mounted on a solid shaft and which rotates at a high circumferential speed. Said rotational movement
20 in connection with a high air through-put converts the through-flowing hot air into extremely fast air vortices which take up the material to be dried, accelerate same and distribute same so finely that a larger surface is generated. After having been dried completely, the
25 aluminium hydroxide particles transposed into a condition of turbulence leave the mill drying unit and are separated from the hot air and the vapour. The circumferential speed of the rotor ranges between 40 - 140 m/sec. The hot air used for drying purposes has a temperature of 150 - 450 °C.
30 It is possible to use conventional mill drying units; for example see Lueger, Lexikon der Technik, volume 48, p. 394.

The ultra-fine hydroxide powder obtained in this way is characterised by a very low oil absorption. As compared to commercially available products, the oil absorption of the inventive product is reduced by at least 20%. This applies
5 to a comparison with products which comprise a comparable degree of fineness and a comparable or even larger specific surface according to BET (Brunnauer, Emmet, Teller method).

In the case of the aluminium hydroxide in accordance with
10 the invention, X-ray diffractometer scans, in addition to the expected crystal modification gibbsite, show a boehmite percentage of approximately 1%. This is the case if the hot air temperature selected for mill drying is $>270^{\circ}\text{C}$. The commercially available fine-crystalline aluminium
15 hydroxides used for comparative purposes are usually pure gibbsites. In the inventive product, the boehmite percentage is largely found on the surface of the particles.

Water absorption was tested according to Baumann (H.
20 Baumann, Fette, Seifen, Anstrichmittel, 68, 1966, 741-743). This method was used in order to differentiate minerals and mineral filler materials according to polarity and hydrophilicity. More particularly, the method is used for assessing the surface coating of inorganic filler materials
25 with organic additives as to whether the respective filler material was sufficiently hydrophobized. Substances which absorb a big quantity of water per mass unit of filler material are more hydrophilic than those which absorb smaller quantities of water. The inventive flame retardant
30 agents were compared with commercially available standard products. The water absorption rate of aluminium hydroxides in accordance with the invention is 35% and, respectively,

27% lower than that of commercially available comparative products.

The products produced in accordance with the above-mentioned method could be incorporated into polymers more easily and led to better rheological properties of the mixture than comparative products commercially available so far. It was recognized that the mineral filler materials used were more hydrophobic than the filler materials used so far. Surprisingly, the new filler materials are more compatible with the polymer matrix. The lower the degree of oil absorption, the less polymer is needed for wetting the mineral surface. If less polymer is used for wetting the mineral surface, more polymer chains are available inside the matrix for mutual sliding off. In the final analysis, polymer mixtures with filler materials with a low oil index have lower viscosity values than those produced with filler materials having a high oil absorption index. This applies to polymer melts and to reactive resins which are liquid at room temperature, prior to complete curing, even at high filler levels of up to 80 %.

If the product characterised in this way is mixed into an unsaturated polyester resin (abbreviated UP resin), much lower viscosity values are identified than in case of mixtures containing commercially available comparative products at the same concentration. Accordingly, the inventive product is also suitable for producing mixtures with a higher filler level, which still flow very well. If relative viscosity values are compared, the viscosity of the inventive product with a filler level of 50% by weight is approximately 60% lower than that of standard products.

If the aluminium hydroxide dried in accordance with the above-mentioned method is incorporated into a thermoplastic polymer matrix via melt methods, the resulting compound comprises the expected low melt viscosities determined as melt indices. This effect is achieved with and without the use of standard low-molecular coupling agents, as illustrated by the concentration series tested with reference to a Ethyl-vinyl acetate copolymer (abbreviated: EVA or EVA-copolymer) and to an amino-silane (Example 4). The tests were carried out with fixed relationships of filler material and polymer and varying percentages of amino-silane. The inventive product was compared with commercially available standard products. As expected, the product in accordance with the invention comprises a higher melt flow index over the entire range. The increase in percentages with reference to the standard product ranged between 20 and 40%.

On the basis of the described aluminium hydroxide, polymer compounds in the form of simple basic polymer mixtures were produced, having technical significance for the application as halogen-free flame retardant cable sheathing or cable insulating material. Apart from the very advantageous mechanical and flame proofing properties, the resulting polymer compounds comprise excellent melt flow properties. As compared with standard products of the group of commercially available ultra-fine crystalline aluminium hydroxides, said high melt flow index and said viscosity respectively are particularly striking.

Said greatly improved melt flow properties of compounds with a high filler level constitute a basic precondition for achieving high extrusion speeds when applying said flame retardant materials to electrical conductors. Example 5 9) contains the results obtained when extruding two plastics compounds onto a copper conductor. When processing the mixture containing the inventive product, it was found that as compared to the compound containing the commercially available, the former comprises a lower melt 10 pressure and a lower melt temperature while the remaining parameters remain constant, i.e. the extruder screw speed and the extraction speed. For the person entrusted with the extrusion process, this means that, by increasing the screw speed it is possible to use this mixture at higher 15 extrusion and extraction speeds when producing insulated wires and cables.

Optionally, in connection with low melt viscosities and standard high filler levels, it is possible to increase 20 the filler level further in order to achieve even better flame retardant polymer compounds. However, the melt viscosity and the mechanical properties can be kept at a normal level, which is not possible with standard products.

Below, the invention will be explained in greater detail 25 with reference to several examples. Examples 1 and 2 refer to inventive products and their production.

Examples 3 to 9 contain comparative examples which 30 demonstrate the advantages of the products in accordance with the invention.

Examples

Example 1) and 2) describe the production of the inventive product.

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Example 1

The filter cake of a finely crystallised aluminium hydroxide with a specific surface of approx. $3\text{m}^2/\text{g}$ and a residual moisture of approx. 50% by weight was introduced
 10 into a mill drying unit through conventional conveying elements. The solid matter introduced amounted to $200\text{kg}/\text{h}$. Hot air with an entering temperature of $270 - 290^\circ\text{C}$ was added. The quantity of air amounted to $5000\text{ Bm}^3/\text{h}$. The rotational speed of the rotor was set at $80\text{m}/\text{sec}$. The dried
 15 product was separated by a sufficiently dimensioned product filter and removed via a rotary valve.

Table 1) summarises the most important properties of the powder obtained in his way and compares same with the
 20 properties of three commercially available flame retardant agents based on ultra-fine aluminium hydroxide. The comparative product B was obtained on the basis of the same filter-moist ultra-fine hydroxide as the inventive product A.

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The inventive product A and the comparative products B, C and D were subjected to a water absorption test according to Baumann. The device and the test method are described in H. Baumann, GIT-Fachzeitschrift für das Laboratorium, Heft
 30 6, 6. Juni 1967, pp 540-542 and in H. Baumann, Fette, Seifen, Anstrichmittel, 68, 1966, pp 741-743.

Figure 1 shows the water absorption of the flame retardant agents compared as a function of the test duration. After 5 - 15 minutes, the products are saturated with water. A longer test period does not increase the water absorption rate any further. The water absorption rate of the inventive product A is at least 36% lower than that of the comparative products. This value is identical with the oil absorption values. Product A is already saturated at 21% (0.21g oleic acid per 1g filler material) while the commercially available products are saturated at 27 - 35%.

Table 1)

Property	Method	"4m ² /g aluminium hydroxides"			
		Product A	Product B	Product C	Product D
d90 (µm)	Laser granulometry	0.5	0.5	0.6	0.6
d50 (µm)	Laser granulometry	1.2	1.4	1.6	1.6
d10 (µm)	Laser granulometry	2.6	3.2	3.4	5.3
BET (m ² /g)	DIN 66131	3.8	3.1	3.5	4.6
Boehmite (%)	XRD	1%	-	-	-
Moisture (%)	DIN EN ISO 787-2	0.19	0.19	0.24	0.23
Oil absorption (%)		21	27	29	35
DIN EN ISO 787-5					
Water absorption (ml/g)	acc.to Baumann	0.43	0.68	0.68	0.71

d90 describes the grain size value for which applies that 90% of all particles are larger.

5 d50 describes the mean grain diameter and thus the value for which applies that 50% of all particles are larger and 50% of all particles are smaller.

d10 describes the grain size value for which applies that 10% of all particles are larger.

10 Example 2)

The filter cake of a finely crystallised aluminium hydroxide with a specific surface of approx. $5\text{m}^2/\text{g}$ and a residual moisture of approx. 53% by weight was introduced
15 into a mill drying unit through conventional conveying elements. The solid matter introduced amounted to 200kg/h . Hot air with an entering temperature of $250 - 280^\circ\text{C}$ was added. The quantity of air amounted to $5000\text{Bm}^3/\text{h}$. The rotational speed of the rotor was set between 2000-3000 rpm.
20 The dried product was separated by a sufficiently dimensioned product filter and removed via a rotary valve.

Table 2) summarises the most important properties of the powder E obtained in his way and compares same with the
25 properties of the commercially available product F. In addition, Table 2) contains the data of a product G which was produced on the basis of the same filter-moist ultra-fine hydroxide as the inventive product E, but according to the method on which the commercially available product F is
30 based.

The inventive product E and the commercially available products F and as well as product G were subjected to a

water absorption test according to Baumann. Figure 2 shows the water absorption rates of the two filler materials as a function of the test duration. After 5 - 15 minutes, the products are saturated with water. A longer test period does not increase the water absorption rate any further. The water absorption rate of the inventive product E is at least 27% lower than that of the products F and G. This value is identical with the oil absorption values. Product E is already saturated at 24%, product F only at 34%. Product G, too, at 31%, comprises an oil absorption index which is approximately 30% higher than that of the inventive product E.

Table 2)

Property	Method	"6m ² /g aluminium hydroxides"		
		Product E	Product F	Product G
d90 (µm)	Laser granulometry	0.5	0.5	0.6
d50 (µm)	Laser granulometry	0.0	1.1	1.1
d10 (µm)	Laser granulometry	2.6	2.7	2.4
BET (m ² /g)	DIN 66131	6.9	6.0	5.2
Boehmite (%)	XRD	1%	-	-
Moisture (%)	DIN EN ISO 787-2	0.19	0.40	0.26
Oil absorption(%)		24	34	31
DIN EN ISO 787-5				

Water ab-			
sorption(ml/g) acc.to Baumann	0.77	1.00	0.98

5 Example 3)

The inventive product A and the comparative products B, C and D were mixed with Palapreg P17, an unsaturated polyester resin, manufactured by BASF AG. An agitator of type IKA-RE 166 was used for introducing the filler material. Identical quantities of Palapreg P17 and filler material were introduced for 3 minutes at 3500 rpm and subsequently again for 2 minutes at 5500 rpm, to obtain a finely distributed mixture with a filler level of 50 % by weight. The filled resin obtained in this way was thermostated for 2 hours at 22 °C and subsequently measured in a Brookfield RVT viscometer at 20 rpm (using spindle 6). Table 3) compares the results.

20 Table 3)

Flame retardant agent	Absolute viscosity (Pas)	Rel. viscosity
Without	3.81	1
25 Product A	32.4	8.5
Product B	95.2	25.0
Product C	99.0	26.0
Product D	>200	-

30 The viscosity of Product A is by far the lowest. Products B and C are more viscous by the factor 3 and product D,

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Table 4) summarizes the compositions and the most important parameters of a polymer compound based on an EVA copolymer with a vinyl acetate content of 19 % by weight. The flame retardant agents compared are ultra-fine crystalline aluminium hydroxides with a specific surface of

approximately 4m²/g according to BET. The three aluminium hydroxide grades compared with the inventive type are commercially available products.

5 The mixture was produced on a dispersion kneading device of
type LDUK 1.0 manufactured by Werner und Pfleiderer. Test
specimens for the subsequent tests were punched out of
plates produced by compression molding in a "Schwabenth
press" of type Polystat 300S. The mechanical tests
10 according to DIN 53504 were carried out in a tensile test
machine of type Tiratest 2705. The melt flow index to ASTM
D 1238 was determined by the Melt Flow Tester 6942 and the
oxygen index to ISO 4589 (ASTM D 2863) was determined in a
FTA manufactured by Stanton Redcroft.

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Table 4)

	Composition	4.1	4.2	4.3	4.4
	Escorene UL 00119	38.3	38.3	38.3	38.3
20	Dynasylan AMEO	0.4	0.4	0.4	0.4
	Product A	61.3			
	Product B		61.3		
	Product C			61.13	
	Product D				61.3
25	Σ	100	100	100	100
	Tensile strength				
	(MPa)	13.5	13.5	13.5	13.5
	Elongation at				
	break (%)	210	210	193	181
30	LOI (%O ₂)	38.2	37.6	36.3	37.5

	MFI (cm ³ /10 min);				
	21.6 kg/160 °C	1.6	1.1	1.0	1.2
	MFI (cm ³ /10 min);				
5	21.6 kg/190 °C	4.2	3.1	2.6	3.0

Escorene UL00119 is an EVA copolymer manufactured by ExxonMobil.

Dynasytan AMEO is an amino silane manufactured by Degussa
10 AG.

Tensile strength - obtained from stress strain measurements according to DIN 53504.

Elongation at break - obtained from the stress strain measurements according to DIN 53504

15 LOI = limiting oxygen index according to ISO 4589

MFI = melt flow index according to ASTM D 1238.

The comparison shows that the inventive product A exhibits the best values of all products compared. Apart from very advantageous mechanical properties, the melt flow index of formulation 4.1 is at least 35% higher than that of the comparative materials.

Example 6

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Table 5) summarizes the compositions and the most important parameters of a polymer compound based on an EVA copolymer with a vinyl acetate content of 26 % by weight. The flame retardant agents compared are ultra-fine crystalline aluminium hydroxides with a specific surface of approximately 4m²/g according to BET. The three aluminium

hydroxide grades compared with the inventive type are commercially available products.

The compounds and test specimens were produced as described under example 5).

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In this formulation, too, the inventive aluminium hydroxide comprises the highest melt flow index by far. As compared to standard grades, the value is increased by at least 25% (see 5.1 compared with 5.2-5.4).

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Table 5)

	Composition	5.1	5.2	5.3	5.4
	Escorene UL 00226	38.3	38.3	38.3	38.3
15	Dynasylan AMEO	0.4	0.4	0.4	0.4
	Product A	61.3			
	Product B		61.3		
	Product C			61.13	
	Product D				61.3
20	Σ	100	100	100	100
	Tensile strength (MPa)	12.6	12.2	12.0	10.5
	Elongation at rupture (%)	243	256	221	220
25	LOI (%O ₂)	37.1	36.1	36.7	37.1
	MFI (cm ³ /10 min); 21.6 kg/160 °C	3.8	3.0	2.6	3.1
	MFI (cm ³ /10 min); 21.6 kg/190 °C	10.6	8.5	7.0	7.2

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Escorene UL00226 is an EVA copolymer manufactured ExxonMobil.

Example 7)

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Table 6) summarizes the compositions and the most important parameters of a polymer compound based on an EVA copolymer with a vinyl acetate content of 19 % by weight. In the case of this example, ultra-fine crystalline aluminium hydroxides with a specific surface of approximately 6m²/g according to BET were compared. The inventive type was produced in accordance with the method described under example 2). A comparison was carried out with a commercially available aluminium hydroxide grade.

15 The compounds and test specimens were produced as described under example 5).

In the case of this example, too, the inventive Product E comprises the superior melt flow index. Apart from better elongation at break values, the MFI values of the inventive product E - depending on measuring conditions, are increased by at least 68%.

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Table 6)

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Composition	6.1	6.2
Escorene UL 00119	38.3	38.3
Dynasylan AMEO	0.4	0.4
Product E	61.3	
Product F		61.3
Σ	100	100

30

Table 7)

	Composition	7.1	7.2
	Escorene UL 00119	38.3	38.3
5	Dynasylan AMEO	0.4	0.4
	Product E	61.3	
	Product F		61.3
	E	100	100
	Tensile strength		
10	(MPa)	14.9	15.2
	Elongation at		
	rupture (%)	206	184
	LOI (%O ₂)	42.3	40.6
	MFI (cm ³ /10 min);		
15	21.6 kg/160 °C	2.6	1.7
	MFI (cm ³ /10 min);		
	21.6 kg/190 °C	7.3	3.9

Example 9)

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Table 8) summarizes the compositions and the most important parameters of a polymer compound based on a PE/EVA blend (EVA with a vinyl acetate content of 26 % by weight). The flame retardant agents compared are ultra-fine crystalline

25 aluminium hydroxides with a specific surface of approximately 4m²/g according to BET. The three aluminium hydroxide grades compared with the inventive type are the commercially available products as used in examples 4) and 5).

The compounds and test specimens were produced as described under example 5).

The results of this compound confirm once again the findings of an increased melt flow index as identified in the preceding examples.

Table 8)

Composition	8.1	8.2	8.3	8.4
Exon Mobile LL 1004 YB	9.66	9.66	9.66	9.66
Escorene UL 00226	29	29	29	29
Silquest FR-693	0.8	0.8	0.8	0.8
Silquest PA-826	0.30	0.30	0.30	0.30
Interox TMCH-75-AL	0.04	0.04	0.04	0.04
Irganox 1010	0.20	0.20	0.20	0.20
Product A	60			
Product B		60		
Product C			60	
Product D				60
Σ	100	100	100	100
Tensile strength				
(MPa)	8.5	8.7	8.6	7.4
Elongation at				
rupture (%)	200	187	143	118
LOI (%O ₂)	36.8	35.6	33.4	33.5
MFI (cm ³ /10 min);				
21.6 kg/160 °C	6.8	5.2	5.1	5.0

Exxon Mobile LL 1004 YB is a LLDPE of ExxonMobile
 Silquest FR-693 is a vinyl silane ester of Osi Specialities
 Silquest PA-826 is a vinyl-modified polydimethylsiloxane
 Interlox TMCH-75-AL is a 75% solution of tert. amylperoxy-
 5 pivalate in aliphatics, manufactured by Peroxid Chemie
 Irganox 1010 is a thermo-stabiliser of Ciba SC
 (pentaerythritol tetrakis3-(3.5-di-tert-butyl-4-
 hydroxyphenyl) proprionate)

10 Example 10)

The comparative product for the subsequent tests was the
 product with the best comparative values according to Table
 8).

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Table 9) shows the results of the stress strain tests and
 the melt flow indices of the compounds of the formulations
 8.1 and 8.2 which were produced by a method which was
 modified as compared to example 9).

20 In this case, the polymer mixture was produced in a Buss-
 ko-kneader of type MDK/E 46-11D. Test specimens for the
 mechanical tests were punched out of extruded strips
 produced on a single-screw extruder (ED 30-GL manufactured
 by Extrudex).

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With this production method, both the mechanical values and
 the melt flow indices have improved as compared to the
 values mentioned in Table 7). In this case, too, the high
 MFI of the compound containing the inventive product has to
 30 be emphasized.

Table 9)

5	Flame retardant agent used	Tensile strength (MPa)	Elong. at rupture (%)	MFI (cm ³ /10min) 21.6kg/160°C
	Product A	10.2	258	9.4
	Product B	10.4	264	5.9

10 The compounds produced in this way were subjected to melt-rheological measurements in a capillary rheometer (Bohlin, type Rosand RH7-2, measuring temperature 150 °C). Figure 4) shows the shear viscosity as a function of the shear rate.

15 In accordance with the MFI values, the composition of the inventive product A, over the entire shear speed range, comprises a lower melt viscosity than the comparative product B.

20 In addition, both compounds were extruded on a thin round copper conductor with a cross-section of 0.5 mm². Said tests were carried out on a Francis Shaw Extruder provided with a BM screw ("Brevet Mailler" = Maillefer patent) The most important parameters are listed in Table 10).

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The compound containing the aluminium hydroxide in accordance with the invention, while the extraction and extrusion temperatures remain the same, can be applied to the copper conductor at a lower pressure and at a lower melt temperature. Vice versa: an increased extraction speed of the insulated copper wire can be achieved by increasing the rotational screw speed to a value in excess of 30 rpm

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and thus by increasing the melt pressure and melt temperature, for example to the level which sets itself in the case of the compound containing the comparative product B and at a rotational screw speed of 30 rpm. However, the test equipment on which the described tests were carried out was not designed for higher extraction speeds.

Table 10)

Filler material Set parameters Parameters occurring during extrusion

	Extraction speed (m/min)	screw speed (rpm)	Nozzle dia. (inner/out.) (mm)	Melt temp. (°C)	Melt pressure (bar)
Product A	650	30	0.85/1.4	151	750
Product B	650	30	0.85/1.4	168	800